

**Attachment A**

European Patent Application No. 01 100 537.8

# Empfangsbescheinigung / Receipt for documents / Recepissé de documents

(Liste der diesem Antrag beigefügten Unterlagen)

(Checklist of enclosed documents)

(Liste des documents annexés à la présente requête)

Es wird hiermit der Empfang der unten bezeichneten Dokumente bescheinigt / Receipt of the documents indicated below is hereby acknowledged / Nous attestons le dépôt des documents désignés ci-dessous

Wird im Falle der Einreichung der europäischen Patentanmeldung bei einer nationalen Behörde diese Empfangsbescheinigung vom Europäischen Patentamt überantwortet, so ist sie als Mitteilung gemäß Regel 24(4) anzusehen (siehe Feld RENA). Nach Erhalt der Mitteilung nach Regel 24(4) sind alle weiteren Unterlagen, die die Anmeldung betreffen, nur noch unmittelbar beim EPA einzureichen. / If this receipt is issued by the European Patent Office and the European patent application was filed with a national authority it serves as a communication under Rule 24(4) (see Section RENA). Once the communication under Rule 24(4) has been received, all further documents relating to the application must be sent directly to the European Patent Office. / Si, en cas de dépôt de la demande de brevet européen auprès d'un service national, l'Office européen des brevets délivre le présent récépissé de documents, ce récépissé est réputé être la notification visée à la règle 24(4) (cf. rubrique RENA). Dès que la notification visée à la règle 24(4) a été reçue, tous les autres documents relatifs à la demande doivent être adressés directement à l'OEB.

15. JAN. 2001  
E. Blum & Co.  
Vorderberg 11  
CH-8044 Zürich

Nur für nationalen Gebrauch / Only for internal / Seul pour usage national	
Datum / Date	Europäisches Patentamt European Patent Office Office européen des brevets D-80298 München
	A. Kollner

Unterschrift / Avisstempel / Signature / Official stamp / Signature / Cachet officiel

01100537.8

10. 01. 01

Anmeldenummer / Application No. / N° de la demande

Tag des Eingangs (Regel 24(2)) / Date of receipt  
(Rule 24(2)) / Date de réception (règle 24(2))

DREC

Zeichen des Anmelders/Vertreters / Applicant's/ Representative's ref. / Référence du demandeur ou du mandataire

AREF

Nur nach Einreichung der Anmeldung bei einer nationalen Behörde: / Only after filing of the application with a national authority: /  
Seulement après le dépôt de la demande auprès d'un service national:

Tag des Eingangs beim EPA (Regel 24(4)) / Date of receipt at  
EPO (Rule 24(4)) / Date de réception à l'OEB (règle 24(4))

RENA

A. Anmeldungsunterlagen und Prioritätsbeleg(e) / Application documents and priority document(s) / Pièces de la demande et document(s) de priorité

1. Beschreibung (ohne Sequenzprotokollteil) / Description (excluding sequence listing part) / Description (sauf partie réservée au listage des séquences)

2. Patentansprüche / Claim(s) / Revendication(s)

3. Zeichnung(en) / Drawing(s) / Dessin(s)

DRAW 1 #

4. Sequenzprotokollteil der Beschreibung / Sequence listing part of description / Partie de la description réservée au listage des séquences

5. Zusammenfassung / Abstract / Abrégé

6. Übersetzung der Anmeldungsunterlagen / Translation of the application documents / Traduction des pièces de la demande

7. Prioritätsbeleg(e) / Priority document(s) / Document(s) de priorité

8. Übersetzung des (der) Prioritätsbelegsbeleg(e) / Translation of priority document(s) / Traduction du (des) document(s) de priorité

B. Der Anmeldung in der eingereichten Fassung liegen folgende Unterlagen bei: / This application as filed is accompanied by the items below: / A la présente demande sont annexées les pièces suivantes:

1. Einzelvollmacht / Specific authorisation / Pouvoir particulier

2. Allgemeine Vollmacht / General authorisation / Pouvoir général

3. Erfindermann / Designation of inventor / Désignation de l'inventeur

4. Früherer Recherchebericht / Earlier search report / Rapport de recherche antérieure

5. Gebührenzahlungsvordruck (EPA Form 1010) / Voucher for the settlement of fees (EPO Form 1010) / Bordereau de règlement de taxes (OEB Form 1010)

6. Scheck (nicht bei Einreichung bei den nationalen Behörden) / Cheque (not when filing with national authorities) /

Chèque (pas de chèque en cas de dépôt auprès des services nationaux)

7. Datenträger für Sequenzprotokoll / Data carrier for sequence listing /

Support de données pour liste de séquences

8. Zusatzblatt / Additional sheet / Feuille additionnelle

9. Sonstige Unterlagen (bitte hier spezifizieren) / Other documents (please specify here) / Autres documents (veuillez préciser)

	Stückzahl / Number of copies / Nombre d'exemplaires	Blattzahl* eines Stücks / Number of sheets* in each copy / Nombre de feuilles* par exemplaire	Gesamtzahl der Abbildungen* / Total number of figures* / Nombre total de figures*
3	7		
3	2		
3	1		1
0			
3	1		

48

SEOL 4

Währung Betrag / Currency Amount / Montant  
(Ausführung freigesetzt / optional / facultatif)

EUR 1097.--

A method for producing a structure using nanoparticles

The present invention relates to a method for producing a structure using nanoparticles according to  
5 the preamble of claim 1 as well as to structures produced by this method and an application thereof.

The term "nanoparticles" designates particles having a diameter well in the submicron range. It has been known that such particles start to exhibit thermo-  
10 physical properties substantially different from bulk materials. In particular, the melting point starts to decrease substantially for particle diameters e.g. below 100 nm, and in particular below 10 nm. Nanoparticles of gold show e.g. a melting point of 300 to 400 °C at a diameter of 2.5 nm while the bulk melting point of gold is 1063 °C.

In WO 00/10197 this effect is exploited for producing copper structures on a semiconductor wafer at low temperatures. A suspension of copper nanoparticles in  
20 a liquid is applied to a semiconductor chip. After evaporation of the solvent, nanoparticles are concentrated in recesses in the wafer surface and the wafer is heated above the particles' melting point to sinter or melt them. This method takes advantage of the comparatively  
25 low melting point of the particles, but it requires the presence of suitable recesses in the surface of the substrate.

The problem to be solved by the present invention is to provide a method for preparing fine structures using nanoparticles without requiring dedicated recesses on the substrate.  
30

This problem is solved by the method of claim 1. Accordingly, the nanoparticles are molten at least in part by exposition to laser light, whereupon they are solidified for forming a solid structure in those places where the nanoparticles were heated up by the laser.  
35 This allows to use the laser to define the structure.

Preferably, the laser light is focussed in a focal point, which is moved in respect to the substrate, thereby forming a solidified line of bulk material from the nanoparticles.

5 Preferably, the nanoparticles are mixed with a liquid to form a suspension which can then be applied to the substrate, e.g. using an ink jet printer device.

10 The average diameter of the nanoparticles should be sufficiently small for reducing the melting point of the nanoparticles substantially below the bulk melting point. For most materials the average diameter should be less than 100 nm, in particular less than 10 nm, preferably between 2 nm and 5 nm. The nanoparticles can be of any material being suited for sintering or re-melting upon laser irradiation. In particular, they can 15 be of a metal, such as gold.

20 Further preferred embodiments of the invention as well as applications thereof are disclosed in the dependent claims as well as in the following description. This description makes reference to Fig. 1, which shows a schematic drawing of a set-up for preparing a structure 25 from nanoparticles.

Fig. 1 shows a diagram of a preferred apparatus for generating a structure from nanoparticles on a substrate 1, which can e.g. be a semiconductor wafer. A droplet generator 2 is provided for generating a controlled, directed series of drops 3 of a solid in liquid suspension directed onto the substrate. The suspension consists, in a preferred embodiment, of gold nanoparticles in an organic solvent.

30 The drops 3 are deposited on substrate 1 to form a layer 4 thereon.

The beam of a laser 5 is focussed in a focal point 6 on layer 4 using suitable focusing optics 7. The 35 radiation energy of the laser light is absorbed by the nanoparticles, leading to a temperature increase above the melting point of the particles. The generated heat

evaporates the solvent and melts the nanoparticles at least partially. When the heated nanoparticles are moved away from focal point 6, they cool down and solidify, leaving a solid structure 8.

5 While drops 3 are being deposited and laser 5 sinters or melts the particles into the solid structure, substrate 1 is being moved in respect to laser 5 and droplet generator 2. For this purpose, substrate 1 can e.g. be displaced by a positioning stage (not shown),  
10 while laser 5 and droplet generator 2 remain stationary.

Preferably, the drops 3 generated by droplet generator 2 impinge on substrate 1 at the position of focal point 6, which makes it possible to create a line shaped structure 8 along any direction.

15 Once structure 8 has solidified, any excess solvent and not sintered nanoparticles are removed, e.g. by washing. This post-processing step can be avoided by depositing a line-structure that is smaller than the focal point of the laser so that the deposit solvent is  
20 evaporated in its entirety.

The operation of drop generator 2 and laser 5 and the displacement of substrate 1 are preferably controlled by a computer 10.

For monitoring the formation of the structure 25 8, the apparatus can further be provided with a monitoring system, which comprises a stroboscope 11, a camera with microscope lens 12 and a framegrabber 13. The stroboscopic light source 11 is triggered e.g. in synchronicity with the release of the drops 3, thereby generating a standing picture of the drops arriving at focal point 6  
30 in framegrabber 13.

In the following, some aspects of the procedure are described in more detail.

35 Nanoparticles, suspension:

The nanoparticles are preferably made of metal for forming a metallic structure. Gold has been

found an especially suited material. As mentioned above, nanoparticles of gold show a melting point of 300 to 400°C at a diameter of 2.5 nm, which allows to form the desired structure at moderate temperatures.

5       The nanoparticles can also be made of a non-metallic material. In particular, the present method also allows to form ceramic structures. Of particular interest are superconductive ceramics, which could be sintered with the present process without creating the excessive 10 thermal stress that is responsible for the prohibitively brittle behaviour of superconductive ceramic components.

15      A preferred "solvent" or, more accurately, suspension-fluid for the nanoparticles is toluene. Toluene has good wetting properties and its viscosity is suited for generating small droplets. Further preferred solvents are other organic solvents, such as terpineol or xylene, or water.

#### Droplet generator:

20      The droplet generator 2 can be any device suited for a controlled generation of the drops 3. Preferred is the application of a drop on demand device where a volume of the suspension is compressed by piezoelectric or thermal compression, thereby squirting one or 25 more drops of the suspension through an opening onto the substrate. Piezoelectric compression or any other isothermal mechanical or electromechanical compression is preferred because it is suited for any suspension, while the evaporation process required in thermal compression 30 (bubble jet method) can lead to contamination or clogging.

#### Laser light:

35      The wavelength of the laser light and the intensity at focal point 6 have to be selected according to the properties of the nanoparticles as well as according to the desired heating rate. For best efficiency, at

least 80% of the laser light should be absorbed in layer 4.

Preferably, the exponential absorption coefficient of the suspension for the laser light is even higher, at least  $0.1 \mu\text{m}^{-1}$ , in particular at least  $1 \mu\text{m}^{-1}$ , which ensures that most of the laser light is absorbed close to the surface of layer 4. It has been found that the heat is transported through the whole depth of the layer, sintering or melting all nanoparticles in focal point 6.

The wavelength of the laser light is preferably chosen to be in a region of high absorption of the suspension. The laser can either be operated in continuous or pulsed mode.

The diameter of focal point 6 must be sufficiently small for forming even the finest parts of the desired structure. A typical diameter is less than 500  $\mu\text{m}$ , preferably less than 100  $\mu\text{m}$ .

Typical average laser powers at a displacement speed in the order of 1  $\text{mm/s}$  are in the order of 0.2 W to 2 W with a focal point diameter of 100  $\mu\text{m}$ , resulting in intensities in the order of 25 to 250  $\text{W/mm}^2$ .

#### Example:

In a preferred example, gold nanoparticles with a mean average size of 2 to 5 nm were suspended in toluene. The mass-fraction of gold in the solution was 40% of the total weight.

Droplets were generated with a drop on demand piezoelectric jetting device from Microfab Inc. This piezoelectric device consists of a reservoir and a capillary glass tube filled with the suspension. A piezoelectric material is deposited on the outer surface of the glass capillary. When a voltage pulse series is applied to the piezoelectric material, a volumetric change is induced to the fluid (and a corresponding pressure wave is generated within it) and a drop 3 will be ejected.

The drops 3 were deposited to form layer 4 as a line on a silicon wafer substrate by moving the substrate continuously at a speed of 1 mm/s with a positioning stage. The deposited layer 4 was simultaneously cured 5 by light from an Argon ion laser at a wavelength of 488 nm, where the slurry had an absorption of less than 1  $\mu\text{m}^{-1}$ . The focal point 6 was located right behind the point where the drops impinged on the substrate 1. It had a diameter of approximately 100  $\mu\text{m}$ .

10 After cooling, the remaining structure consisted of solid, continuous, electrically conducting gold lines with an electrical conductance at least as good as that of bulk gold. The lines had a typical width of 60 - 100  $\mu\text{m}$ .

15

In the example mentioned above, substrate 1 was a silicon wafer. Other types of substrates can be used as well, such as substrates of glass or ceramic.

20 For expediting the melting or sintering of the nanoparticles, the substrate and/or the suspension can be heated to a temperature below the melting point of the nanoparticles, thereby decreasing the amount of energy required from the laser.

25 In the above examples, the liquid layer 4 has been formed by applying the drops 3 generated by droplet generator 2. Instead of a drop-wise application of the suspension, other coating methods, such as spin coating, can be used for producing layer 4. Again, the laser light is then used for forming the desired structure.

30 Instead of being present in the form of a regular suspension (i.e. a solid in liquid suspension), layer 4 may also be formed by a "solid suspension", i.e. the nanoparticles can be suspended in a solid matrix, e.g. by solidifying the "solvent" after spin coating by 35 temperature decrease or partial evaporation. Alternatively, the nanoparticles can be suspended in a gas.

The heating and curing of the nanoparticles with laser light can take place while layer 4 is being formed, such as shown in the example above. It can also take place after the formation of layer 4.

5

The method described here can be used for forming any type of structure. Examples are conducting lines for interconnections on or to a semiconductor chip or for connecting a semiconductor chip to a substrate or 10 to connector pins, metallic or non-metallic parts of Micro Electromechanical Systems (MEMS) or superconducting structures.

A primary application of the present invention is for constructing gold lines for interconnections in electronics manufacturing, ranging from chip assembly packaging to flat panel display construction. The critical benefit to be harvested from the low melting and bonding temperatures of the gold nanoparticles is two-fold: First, the printing of gold microline interconnections with a at-demand microdroplet generation technique is possible because one deals with a room temperature nanosuspension facilitating the application of piezoelectric ceramics with Curie temperatures of only a few hundred degrees Celsius. This would be impossible with molten gold at temperatures exceeding 1063 °C. Second, at the droplet deposition end, excess thermal stress and melting or burning of sensitive chip structures can be avoided. The method can be used under normal atmosphere environment yielding a fast, user friendly and cost effective interconnection manufacturing process appropriate for use in combination with a variety of delicate substrate materials.

**Claims**

1. A method for producing a structure on a substrate (1) comprising the step of applying nanoparticles of a material to form the structure (1) and characterized by the steps of melting the nanoparticles at least partially by exposition to laser light and solidifying the molten nanoparticles for forming the structure (8).  
10        2. The method of claim 1 comprising the steps of focussing the laser light in a focal point (6) and translating the focal point (6) in respect to the substrate (1) for forming the structure.
- 15        3. The method of claim 2 wherein the focal point (6) has a diameter of less than 500 µm, in particular less than 100 µm.
- 20        4. The method of one of the claims 2 or 3 wherein the substrate (1) is moved for generating the structure.
- 25        5. The method of one of the preceding claims comprising the step of applying a suspension of the nanoparticles in a liquid to the substrate (1), and in particular of forming a layer (4) of the suspension on the substrate (1).
- 30        6. The method of claim 5 wherein the suspension is applied in drops (3) to the substrate (1) using a droplet generator (2).
- 35        7. The method of claim 6 comprising the step of generating the drops (3) by compressing a volume of the suspension by piezoelectric or thermal compression and thereby squirting the drops through an opening onto the substrate.
- 40        8. The method of one of the claims 2 to 4 and of one of the claims 5 to 7 wherein the drops (3) are deposited on the substrate (1) at the focal point (6).

9. The method of one of the claims 5 to 8 wherein the liquid is selected from the group comprising toluene, terpineol, xylene and water.

10. The method of one of the claims 5 to 9  
5 wherein an exponential absorption coefficient of the laser light in the suspension is at least  $0.1 \mu\text{m}^{-1}$ , in particular at least  $1 \mu\text{m}^{-1}$ .

11. The method of one of the claims 5 to 10  
10 wherein the suspension is deposited as a layer (4) on the substrate (1), wherein at least 80% of the laser light is absorbed in the layer (4).

12. The method of one of the preceding claims wherein the nanoparticles are of a metal, in particular of gold.

15. 13. The method of one of the preceding claims wherein an average diameter of the nanoparticles is sufficiently small for reducing a melting point of the nanoparticles substantially below a bulk melting point of the material, and in particular wherein the average diameter  
20 is less than 100 nm, in particular less than 10 nm, preferably between 2 nm and 5 nm.

14. The method of one of the preceding claims wherein the structure is a superconducting ceramic material.

25. 15. The method of one of the preceding claims further comprising the step of observing the production of the structure using a stroboscopic light source (11) and a camera (12), and in particular wherein the stroboscopic light source (11) is triggered in synchronicity  
30 with the application of drops (3) of a suspension of the nanoparticles to the substrate (1).

16. A structure producible by the method of one of the preceding claims.

35. 17. Application of the method of one of the claims 1 - 15 for the production of electrical interconnections on and/or to semiconductor chips.

### Abstract

For forming a fine structure of a desired material, nanoparticles of the same material are prepared  
5 in a suspension. A layer (4) of the suspension is applied to a substrate (1). Part of the layer (4) is exposed to laser light for melting the nanoparticles at least partially. Upon solidification, the molten particles are  
10 sintered together to form the desired structure. Due to the low melting point of nanoparticles as compared to the melting point of bulk material, this procedure avoids damage to the substrate and provides a better control over the structure generation process. It can be used for generating metallic and non-metallic structures on various substrates.  
15

(Fig. 1)

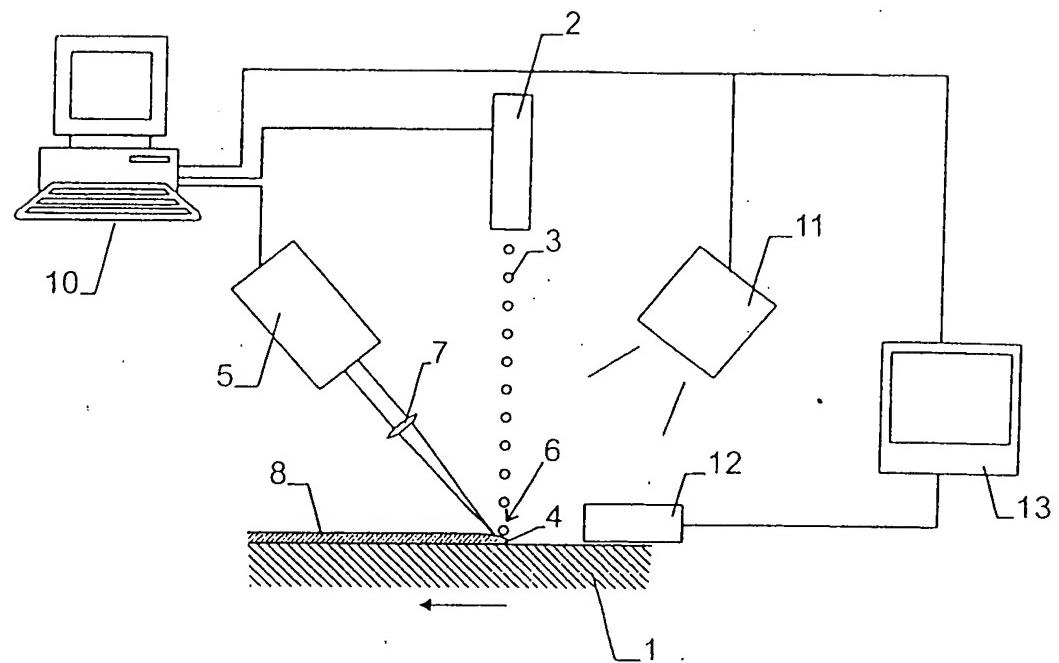


Fig. 1



# Antrag auf Erteilung eines europäischen Patents / Request for grant of a European patent / Requête en délivrance d'un brevet européen

Bestätigung einer bereits durch Telefax eingereichten Anmeldung / Confirmation of an application already filed by facsimile / Confirmation d'une demande déjà déposée par télifax  
Wenn ja, Datum der Übermittlung des Telefax und Name der Einreichungsbehörde / If yes, facsimile date and name of the authority with which the documents were filed / Si oui, date d'envoi du télifax et nom de l'autorité de dépôt

Ja / Yes / Oui

Datum / Date

Behörde / Authority / Autorité

Nur für amtlichen Gebrauch / For official use only / Cadre réservé à l'administration

Anmeldenummer / Application No. / N° de la demande	MKEY	1	
Tag des Eingangs (Regel 24(2)) / Date of receipt (Rule 24(2)) / Date de réception (règle 24(2))	DREC	2	
Tag des Eingangs beim EPA (Regel 24(4)) / Date of receipt at EPO (Rule 24(4)) / Date de réception à l'OEB (règle 24(4))	RENA	3	
Anmeldetag / Date of filing / Date de dépôt		4	

Tabulatoren-Positionen / Tabulation marks / Arrêts de tabulation

Es wird die Erteilung eines europäischen Patents und gemäß Artikel 94 die Prüfung der Anmeldung beantragt / Grant of a European patent, and examination of the application under Article 94, are hereby requested / Il est demandé la délivrance d'un brevet européen et, conformément à l'article 94, l'examen de la demande

EXAM 4

5

Prüfungsantrag in einer zugelassenen Nichtamtssprache (siehe Merkblatt II, 5); / Request for examination in an admissible non-EPO language (see Notes II, 5); / Requête en examen dans une langue non officielle autorisée (voir notice II, 5).  
Si richiede di esaminare la domanda ai sensi dell'art. 94.

Zeichen des Anmelders oder Vertreters (max. 15 Positionen) / Applicant's or representative's reference (maximum 15 spaces) / Référence du demandeur ou du mandataire (max. 15 caractères ou espaces)

AREF

6

04527EP

Anmelder / Applicant / Demandeur

Name / Nom

Anschrift / Address / Adresse

APPR 01 #	
# DEST #	

7

Eidgenössische Technische Hochschule Zürich  
Rämistrasse 101  
CH-8092 Zürich  
Switzerland

8

9

10 CH

11 CH

12

13

14

15 Blum Rudolf E.

Zustellanschrift / Address for correspondence / Adresse pour la correspondance

PADR	
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Staat des Wohnsitzes oder Sitzes / State of residence or of principal place of business / État du domicile ou du siège

Staatsangehörigkeit / Nationality / Nationalité

Telefon / Telephone / Téléphone

Telex / Téléx

Telefax / Fax / Télifax

Weiterer(r) Anmelder auf Zusatzblatt / Additional applicant(s) on additional sheet / Autre(s) demandeur(s) sur feuille additionnelle

Vertreter / Representative / Mandataire

Name / Nom

(Nur einen Vertreter angeben, der in das europäische Patentregister eingetragen ist und an den zugestellt wird / Name only one representative who is to be listed in the Register of European Patents and to whom notification is to be made / N'inclure qu'un seul mandataire, qui sera inscrit au Répertoire européen des brevets et auquel signification sera faite)

FREP 01		#		! # #
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Geschäftsanschrift / Address of place of business / Adresse professionnelle

16 E. Blum & Co.  
Vorderberg 11  
CH-8044 Zürich  
Switzerland

17

0041 1 261 54 54

Telefon / Telephone / Téléphone



<p>Falls das biologische Material nicht vom Anmelder, sondern von einem Dritten hinterlegt wurde: / Where the biological material has been deposited by a person other than the applicant: / Lorsque la matière biologique a été déposée par une personne autre que le demandeur:</p> <p>Ermächtigung nach Regel 28(1)d) / Authorisation under Rule 28(1)(d) / L'autorisation en vertu de la règle 28(1)d)</p> <p>ist beigefügt / is enclosed / est jointe</p> <p>wird nachgereicht / will be filed later / sera produite ultérieurement</p>		<p>28 <input type="checkbox"/> Name und Anschrift des Hinterlegers / Name and address of depositor / Nom et adresse du déposant :</p> <p>28a <input type="checkbox"/></p> <p>28b <input type="checkbox"/></p>
<p>Verzicht auf die Verpflichtung des Antragstellers nach Regel 28(3) in gesonderter Schriftstück / Waiver of the right to an undertaking from the requester pursuant to Rule 28(3) attached</p>		
<p>Gemäß Regel 28(4) wird hiermit mitgeteilt, daß der Zugang zu dem in den Fällen 26 und 27 genannten biologischen Material nur durch Herausgabe einer Probe an einen Sachverständigen hergestellt wird / It is hereby declared under Rule 28(4) that the availability of the biological material referred to in Sections 26 and 27 shall be effected only by the issue of a sample to an expert</p>		
<p><b>Nucleotid- und Aminosäuresequenzen / Nucleotide and amino acid sequences / Séquences de nucléotides et d'acides aminés</b></p> <p>Die Beschreibung enthält ein Sequenzprotokoll nach Regel 27a(1) / The description contains a sequence listing in accordance with Rule 27a(1) / La description contient une liste de séquences selon la règle 27bis(1)</p> <p>Der vorgeschriebene Datenträger ist beigefügt / The prescribed data carrier is enclosed / Le support de données prescrit est joint</p> <p>Es wird hiermit erklärt, daß die auf dem Datenträger gespeicherte Information mit dem schriftlichen Sequenzprotokoll übereinstimmt (Regel 27a(2)) / It is hereby stated that the information recorded on the data carrier is identical to the written sequence listing (Rule 27a(2)) / Il est déclaré par la présente que l'information figurant sur le support de données est identique à celle qui contient la liste de séquences écrite (règle 27bis(2))</p>		<p><b>BIOM 3</b></p> <p><b>SEQ1</b></p>
<p><b>Benennung der Vertragsstaaten und Erklärungen hierzu</b></p> <p>1. Hiermit werden sämtliche Vertragsstaaten des EPÜ benannt, die diesem bei Einreichung dieser Anmeldung angehören*.</p> <p>Mit der Zahlung des siebenfachen Betrags einer Benennungsgebühr gelten die Benennungsgebühren für alle Vertragsstaaten als entrichtet (Art. 2 Nr. 3 GebO).</p> <p>2. Es ist derzeit beabsichtigt, weniger als sieben Benennungsgebühren für folgende Vertragsstaaten zu entrichten (bitte Ländercodes und Vertragsstaaten angeben *):</p>		<p><b>Designation of contracting states and associated declarations</b></p> <p><b>DEST</b></p> <p><input checked="" type="checkbox"/> 1. All states which are contracting states to the EPC at the filing of this application are hereby designated*. Payment of seven times the amount of the designation fee is deemed to constitute payment of the designation fees for all the contracting states (Art. 2, No. 3, RFees).</p> <p><input type="checkbox"/> 2. It is currently intended to pay fewer than seven designation fees for the following contracting states (please indicate country codes and contracting states *):</p>
<p>(1) <input type="checkbox"/> _____</p> <p>(2) <input type="checkbox"/> _____</p> <p>(3) <input type="checkbox"/> _____</p>		<p><b>Désignation d'Etats contractants et déclarations à ce propos</b></p> <p><input checked="" type="checkbox"/> 1. Sont désignés tous les Etats qui sont des Etats contractants de la CBE à la date du dépôt de la présente demande*. Les taxes de désignation sont réputées acquittées pour tous les Etats contractants dès lors qu'un montant correspondant à sept fois la taxe de désignation a été acquitté (art. 2, point 3 du RRT).</p> <p><input type="checkbox"/> 2. Il est actuellement envisagé de payer moins de sept taxes de désignation pour les Etats contractants suivants (prière d'indiquer codes de pays et Etats contractants *):</p> <p>(4) <input type="checkbox"/> _____</p> <p>(5) <input type="checkbox"/> _____</p> <p>(6) <input type="checkbox"/> _____</p>
<p>Es wird beantragt, für die unter Nr. 2 nicht aufgeführten Vertragsstaaten von der Zustellung von Mitteilungen nach Regel 85a(1) und Regel 69(1) abzusehen.</p> <p>3. Wird ein automatischer Abbuchungsauftrag erteilt (Feld 43), so wird das EPA beauftragt, bei Ablauf der Grundfrist nach Artikel 79(2) den siebenfachen Betrag einer Benennungsgebühr abzubuchen. Ist eine Erklärung unter Nr. 2 abgegeben worden, so sollen die Benennungsgebühren nur für die dort angegebenen Vertragsstaaten abgebucht werden, sofern dann EPA nicht bis zum Ablauf der Grundfrist ein anderslauender Auftrag zugeht.</p>		<p>No communications under Rules 85a(1) or 69(1) need be notified in respect of the contracting states not indicated under No. 2.</p> <p>3. If an automatic debit order has been issued (Section 43), the EPO is authorised, on expiry of the basic period under Article 79(2), to debit seven times the amount of the designation fee. If any states are indicated under No. 2, the EPO shall debit designation fees only for those states, unless it is instructed to do otherwise before expiry of the basic period.</p>
		<p><input checked="" type="checkbox"/> Prière de ne pas procéder à la signification des notifications prévues par les règles 85bis(1) et 69(1) pour les Etats contractants n'ayant pas été mentionnés au n° 2.</p> <p><input checked="" type="checkbox"/> 3. Si un ordre de prélèvement automatique est donné (rubrique 43), il est demandé à l'OEB de prélever, à l'expiration du délai normal visé à l'article 79(2), un montant correspondant à sept fois la taxe de désignation. Si une déclaration a été faite au n° 2, les taxes de désignation ne sont prélevées que pour les Etats contractants qui y sont indiqués, sauf instruction contraire reçue par l'OEB avant l'expiration du délai normal.</p>

Verschiedene Anmelder für verschiedene Vertragsstaaten / Different applicants for different contracting states / Différents demandeurs pour différents Etats contractants		33	Name(n) des (der) Anmelder(s) und benannte Vertragsstaaten / Name(s) of applicant(s) and designated contracting states / Nom(s) du (des) demandeur(s) et des Etats contractants désignés															
APPR 02 #																		
<b>Erstreckung des europäischen Patents</b>		34	<b>Extension des effets du brevet européen</b>															
<p>Diese Anmeldung gilt als Antrag, die europäische Patentanmeldung und das darauf erteilte europäische Patent auf alle Nicht-Vertragsstaaten des EPU zu erstrecken, mit denen am Tag ihrer Einreichung „Erstreckungsabkommen“ bestehen (derzeit: Albanien, Litauen, Lettland, Rumänien, Slowenien, ehemalige jugoslawische Republik Mazedonien). Die Erstreckung wird jedoch nur wirksam, wenn die vorgeschriebene Erstreckungsgebühr entrichtet wird.</p>			<p>This application is deemed to be a request to extend the European patent application and the European patent granted in respect of it to all non-contracting states to the EPC with which "extension agreements" exist on the date on which the application is filed (Present situation: Albania, Lithuania, Latvia, Romania, Slovenia, former Yugoslav Republic of Macedonia). However, the extension only takes effect if the prescribed extension fee is paid.</p>															
			<input type="checkbox"/> EXPT															
<p>Es ist derzeit beabsichtigt, die Erstreckungsgebühr für die nachfolgend angekreuzten Staaten zu entrichten: / It is currently intended to pay the extension fee for the states marked below with a cross: / Il est actuellement envisagé de payer la taxe d'extension pour les Etats dont le nom est coché ci-après :</p>																		
Albanien / Albania / Albanie	AL		<input checked="" type="checkbox"/>															
Litauen / Lithuania / Lituanie	LT		<input checked="" type="checkbox"/>															
Lettland / Latvia / Lettonie	LV		<input checked="" type="checkbox"/>															
Rumänien / Romania / Roumanie	RO		<input checked="" type="checkbox"/>															
Slowenien / Slovenia / Slovénie	SI		<input checked="" type="checkbox"/>															
Ehemalige jugoslawische Republik Mazedonien / Former Yugoslav Republic of Macedonia / Ex-République yougoslave de Macédoine	MK		<input checked="" type="checkbox"/>															
			<input type="checkbox"/>															
			<input type="checkbox"/>															
<small>(Platz für Staaten, mit denen nach Drucklegung dieses Formblatts „Erstreckungsabkommen“ in Kraft treten) / (Space for states with which "extension agreements" enter into force after this form has been printed) / (Prévu pour des Etats à l'égard desquels des «accords d'extension» entreront en vigueur après l'impression du présent formulaire)</small>																		
<p>Die Anmeldung ist eine Teilanmeldung / The application is a divisional application / La présente demande constitue une demande divisionnaire</p>		35	<p>Nummer der früheren Anmeldung No. of earlier application Numéro de la demande initiale</p>															
<table border="1"> <tr> <td>DFIL 9</td> <td> </td> <td> </td> <td> </td> <td> </td> <td> </td> <td>#</td> </tr> <tr> <td>PANR</td> <td> </td> <td> </td> <td> </td> <td> </td> <td> </td> <td>#</td> </tr> </table>		DFIL 9						#	PANR						#			
DFIL 9						#												
PANR						#												
<p>Es handelt sich um eine Anmeldung nach Artikel 61(1)(b) / The application is an Article 61(1)(b) application / La présente demande constitue une demande selon l'article 61(1)(b)</p>		36	<p>Nummer der früheren Anmeldung No. of earlier application Numéro de la demande initiale</p>															
<table border="1"> <tr> <td>DFIL 9</td> <td> </td> <td> </td> <td> </td> <td> </td> <td> </td> <td>#</td> </tr> <tr> <td>EANR</td> <td> </td> <td> </td> <td> </td> <td> </td> <td> </td> <td>#</td> </tr> </table>		DFIL 9						#	EANR						#			
DFIL 9						#												
EANR						#												
Patentansprüche / Claims / Revendications		37	<p>Zahl der Patentansprüche Number of claims Nombre de revendications</p>															
			<table border="1"> <tr> <td>7</td> </tr> </table>		7													
7																		
<p>Zur Veröffentlichung mit der Zusammenfassung wird vorgeschlagene Abbildung Nr. /</p>																		

Zusätzliche Abschrift(en) der im europäischen Recherchenbericht angeführten Schriftstücke wird (werden) beantragt /  
 Additional copy(ies) of the documents cited in the European search report is (are) requested /  
 Prière de fournir une (des) copie(s) supplémentaire(s) des documents cités dans le rapport de recherche européenne

ASOC

Es wird die Rückerstattung der Recherchengebühr gemäß Art. 10 GebO beantragt / Refund of the search fee is requested pursuant to Article 10 of the Rules relating to Fees / Le remboursement de la taxe de recherche est demandé en vertu de l'article 10 du règlement relatif aux taxes

Eine Kopie des Recherchenberichts ist beigelegt /  
 A copy of the search report is attached /  
 Une copie du rapport de recherche est jointe

**Automatischer  
Abbuchungsauftrag**

(nur möglich für Inhaber von beim EPA geführten laufenden Konten)

Das EPA wird hiermit beauftragt, fällig werdende Gebühren und Auslagen nach Maßgabe der Vorschriften über das automatische Abbuchungsverfahren vom nebenstehenden laufenden Konto abzubuchen. In bezug auf die Benennungsgebühren wird auf Feld 32.3 verwiesen. Das EPA wird ferner beauftragt, die Erstreckungsgebühren für jeden in Feld 34 angekrouzten „Erstreckungsstaat“ bei Ablauf der Grundfrist zu ihrer Zahlung abzubuchen, sofern ihm nicht bis dahin ein anders-lautender Auftrag zugeht.

Für automatischen Abbuchungsauftrag:  
 For automatic debit order:  
 Pour l'ordre de prélèvement automatique:

**Automatic debit order  
(for EPO deposit account holders only)**

The EPO is hereby authorised, under the Arrangements for the automatic debiting procedure, to debit from the deposit account opposite any fees and costs falling due. With regard to designation fees reference is made to Section 32.3. The EPO is also authorised, on expiry of the basic period for its payment, to debit the extension fee for each of the "extension states" marked with a cross in Section 34, unless it is instructed to do otherwise before expiry of this period.

Anzahl der zusätzlichen Sätze von Abschriften  
 Number of additional sets of copies  
 Nombre de jeux supplémentaires de copies

40

41

42

43

**Ordre de prélèvement  
automatique**

(possibilité offerte uniquement  
aux titulaires de comptes courants  
ouverts auprès de l'OEB)

Par la présente, il est demandé à l'OEB de prélever du compte courant ci-dessous les taxes et frais venant à échéance, conformément à la réglementation relative à la procédure de prélèvement automatique. Pour les taxes de désignation, se reporter à la rubrique 32.3. Il est en outre demandé à l'OEB de prélever, à l'expiration du délai normal prévu pour leur paiement, les taxes d'extension pour chaque «Etat autorisant l'extension» coché à la rubrique 34, sauf instruction contraire reçue avant l'expiration de ce délai.

Nummer des laufenden Kontos /  
 Deposit account number /  
 Numéro du compte courant

Name des Kontoinhabers /  
 Account holder's name /  
 Nom du titulaire du compte

DECA

Eventuelle Rückzahlungen auf das nebenstehende beim EPA geführte laufende Konto / Reimbursement, if any, to EPO deposit account opposite / Remboursements éventuels à effectuer sur le compte courant ci-contre ouvert auprès de l'OEB

DEPA

Die vorgeschriebene Liste über die diesem Antrag beigefügten Unterlagen ergibt sich aus der vorbereiteten Empfangsbescheinigung (Seite 6 dieses Antrages)

The prescribed list of documents enclosed with this request is shown on the prepared receipt (page 6 of this request)

Nummer des laufenden Kontos /  
 Deposit account number /  
 Numéro du compte courant

Name des Kontoinhabers /  
 Account holder's name /  
 Nom du titulaire du compte

2811.0014

E. Blum &amp; Co., Zürich

La liste prescrite des documents joints à cette requête figure sur le récépissé préétabli (page 6 de la présente requête)

Für Angestellte nach Artikel 133(3) Satz 1 mit allgemeiner Vollmacht /  
 For employees under Article 133(3), 1st sentence, having a general authorisation / Pour les employés mentionnés à l'article 133(3), 1<sup>re</sup> phrase, munis d'un pouvoir général

Nr. / No. / n° :

Ort / Place / Lieu

Zurich

Datum / Date 8 January 2001 rw

Kurt Sutter

# Empfangsbescheinigung / Receipt for documents / Recépissé de documents 6

(Liste der diesem Antrag beigefügten Unterlagen)

(Checklist of enclosed documents)

(Liste des documents annexés à la présente requête)

Es wird hiermit der Empfang der unten bezeichneten Dokumente bescheinigt / Receipt of the documents indicated below is hereby acknowledged / Nous attestons le dépôt des documents désignés ci-dessous

Wird im Falle der Einreichung der europäischen Patentanmeldung bei einer nationalen Behörde diese Empfangsbescheinigung vom Europäischen Patentamt übersandt, so ist sie als Mitteilung gemäß Regel 24(4) anzusehen (siehe Feld RENA). Nach Erhalt der Mitteilung nach Regel 24(4) sind alle weiteren Unterlagen, die die Anmeldung betreffen, nur noch unmittelbar beim EPA einzureichen. / If this receipt is issued by the European Patent Office and the European patent application was filed with a national authority it serves as a communication under Rule 24(4) (see Section RENA). Once the communication under Rule 24(4) has been received, all further documents relating to the application must be sent directly to the European Patent Office. / Si, en cas de dépôt de la demande de brevet européen auprès d'un service national, l'Office européen des brevets délivre le présent récépissé de documents, ce récépissé est réputé être la notification visée à la règle 24(4) (cf. rubrique RENA). Dès que la notification visée à la règle 24(4) a été reçue, tous les autres documents relatifs à la demande doivent être adressés directement à l'OEB.

E. Blum & Co.  
Vorderberg 11  
CH-8044 Zürich

Nur für amtlichen Gebrauch / For official use only / Cadre réservé à l'administration

Datum / Date

Unterschrift / Amtsstempel / Signature / Official stamp / Signature / Cachet officiel

Anmeldenummer / Application No. / № de la demande

Tag des Eingangs (Regel 24(2)) / Date of receipt (Rule 24(2)) / Date de réception (règle 24(2))

DREC

Zeichen des Anmelders/Vertreters / Applicant's/ Representative's ref. / Référence du demandeur ou du mandataire

AREF

Nur nach Einreichung der Anmeldung bei einer nationalen Behörde: / Only after filing of the application with a national authority: / Seulement après le dépôt de la demande auprès d'un service national:

Tag des Eingangs beim EPA (Regel 24(4)) / Date of receipt at EPO (Rule 24(4)) / Date de réception à l'OEB (règle 24(4))

RENA

A. Anmeldungsunterlagen und Prioritätsbeleg(e) / Application documents and priority document(s) / Pièces de la demande et document(s) de priorité

	47	Stückzahl / Number of copies / Nombre d'exemplaires	Blattzahl* eines Stücks / Number of sheets* in each copy / Nombre de feuilles* par exemplaire	Gesamtzahl der Abbildungen* / Total number of figures* / Nombre total de figures*
1. Beschreibung (ohne Sequenzprotokollteil) / Description (excluding sequence listing part) / Description (sauf partie réservée au listage des séquences)	3		7	
2. Patentansprüche / Claim(s) / Revendication(s)	3		2	
3. Zeichnung(en) / Drawing(s) / Dessin(s)	3		1	1
4. Sequenzprotokollteil der Beschreibung / Sequence listing part of description / Partie de la description réservée au listage des séquences	0			
5. Zusammenfassung / Abstract / Abrégé	3		1	
6. Übersetzung der Anmeldungsunterlagen / Translation of the application documents / Traduction des pièces de la demande				
7. Prioritätsbeleg(e) / Priority document(s) / Document(s) de priorité				
8. Übersetzung des (der) Prioritätsbelegs(belegs) / Translation of priority document(s) / Traduction du (des) document(s) de priorité				

B. Der Anmeldung in der eingereichten Fassung liegen folgende Unterlagen bei: / This application as filed is accompanied by the items below: / A la présente demande sont annexées les pièces suivantes:

48

1. Einzelvollmacht / Specific authorisation / Pouvoir particulier
2. Allgemeine Vollmacht / General authorisation / Pouvoir général
3. Erfindernennung / Designation of inventor / Désignation de l'inventeur
4. Früherer Recherchebericht / Earlier search report / Rapport de recherche antérieure
5. Gebührenzahlungsvordruck (EPA Form 1010) / Voucher for the settlement of fees (EPO Form 1010) / Bordereau de règlement de taxes (OEB Form 1010)
6. Scheck (nicht bei Einreichung bei den nationalen Behörden) / Cheque (not when filing with national authorities) / Chèque (pas de dépôt auprès des services nationaux)
7. Datenträger für Sequenzprotokoll / Data carrier for sequence listing / Support de données pour liste de séquences
8. Zusatzblatt / Additional sheet / Feuille additionnelle
9. Sonstige Unterlagen (bitte hier spezifizieren) / Other documents (please specify here) / Autres documents (veuillez préciser)

SEOL 4

Währung Betrag / Currency Amount / Monnaie Montant: (Ausfüllung freigestellt / optional / facultatif)

EUR 1097.--

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(19) Europäisches Patentamt  
European Patent Office  
Office européen des brevets



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(12)

## EUROPEAN PATENT APPLICATION

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(71) Applicant: Eidgenössische Technische  
Hochschule Zürich  
8092 Zürich (CH)

(72) Inventors:

- Grigopoulos, Constantine P.,  
Berkeley, Berkeley, CA 94720-1740 (US)

- Bieri, Nicole Renée,  
Sonneneggstrasse 3, 8092 Zürich (CH)
- Poulikakos, Dimos  
Sonneneggstrasse 3, 8092 Zürich (CH)

(74) Representative: Blum, Rudolf Emil Ernst  
c/o E. Blum & Co  
Patentanwälte  
Vorderberg 11  
8044 Zürich (CH)

### (54) A method for producing a structure using nanoparticles

(57) For forming a fine structure of a desired material, nanoparticles of the same material are prepared in a suspension. A layer (4) of the suspension is applied to a substrate (1). Part of the layer (4) is exposed to laser light for melting the nanoparticles at least partially. Upon solidification, the molten particles are sintered together

to form the desired structure. Due to the low melting point of nanoparticles as compared to the melting point of bulk material, this procedure avoids damage to the substrate and provides a better control over the structure generation process. It can be used for generating metallic and non-metallic structures on various substrates.

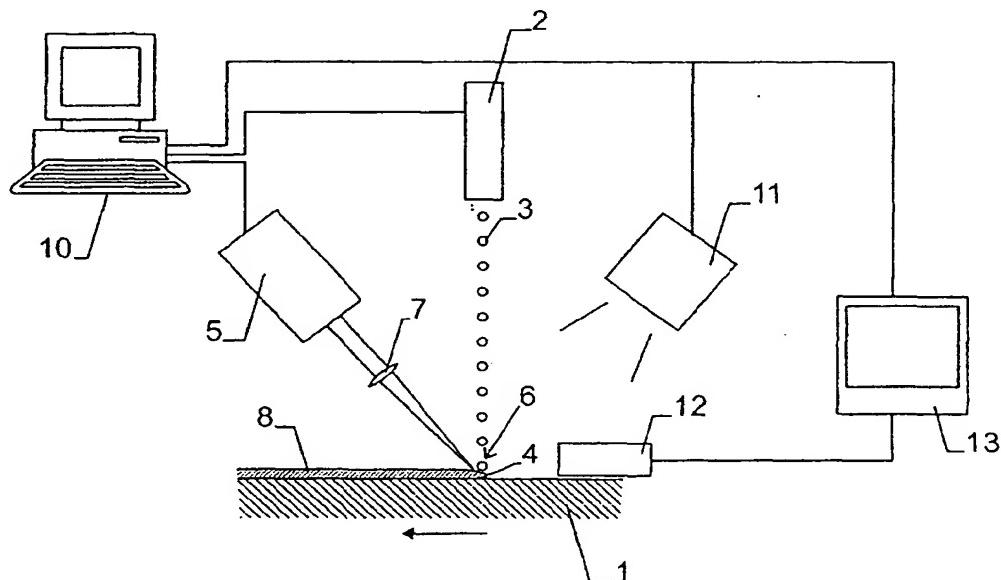


Fig. 1

## Description

[0001] The present invention relates to a method for producing a structure using nanoparticles according to the preamble of claim 1 as well as to structures produced by this method and an application thereof.

[0002] The term "nanoparticles" designates particles having a diameter well in the submicron range. It has been known that such particles start to exhibit thermophysical properties substantially different from bulk materials. In particular, the melting point starts to decrease substantially for particle diameters e.g. below 100 nm, and in particular below 10 nm. Nanoparticles of gold show e.g. a melting point of 300 to 400 °C at a diameter of 2.5 nm while the bulk melting point of gold is 1063 °C. [0003] In WO 00/10197 this effect is exploited for producing copper structures on a semiconductor wafer at low temperatures. A suspension of copper nanoparticles in a liquid is applied to a semiconductor chip. After evaporation of the solvent, nanoparticles are concentrated in recesses in the wafer surface and the wafer is heated above the particles' melting point to sinter or melt them. This method takes advantage of the comparatively low melting point of the particles, but it requires the presence of suitable recesses in the surface of the substrate.

[0004] The problem to be solved by the present invention is to provide a method for preparing fine structures using nanoparticles without requiring dedicated recesses on the substrate.

[0005] This problem is solved by the method of claim 1. Accordingly, the nanoparticles are molten at least in part by exposition to laser light, whereupon they are solidified for forming a solid structure in those places where the nanoparticles were heated up by the laser. This allows to use the laser to define the structure.

[0006] Preferably, the laser light is focussed in a focal point, which is moved in respect to the substrate, thereby forming a solidified line of bulk material from the nanoparticles.

[0007] Preferably, the nanoparticles are mixed with a liquid to form a suspension which can then be applied to the substrate, e.g. using an ink jet printer device.

[0008] The average diameter of the nanoparticles should be sufficiently small for reducing the melting point of the nanoparticles substantially below the bulk melting point. For most materials the average diameter should be less than 100 nm, in particular less than 10 nm, preferably between 2 nm and 5 nm. The nanoparticles can be of any material being suited for sintering or re-melting upon laser irradiation. In particular, they can be of a metal, such as gold.

[0009] Further preferred embodiments of the invention as well as applications thereof are disclosed in the dependent claims as well as in the following description. This description makes reference to Fig. 1, which shows a schematic drawing of a set-up for preparing a structure from nanoparticles.

[0010] Fig. 1 shows a diagram of a preferred apparatus for generating a structure from nanoparticles on a substrate 1, which can e.g. be a semiconductor wafer. A droplet generator 2 is provided for generating a controlled, directed series of drops 3 of a solid in liquid suspension directed onto the substrate. The suspension consists, in a preferred embodiment, of gold nanoparticles in an organic solvent.

[0011] The drops 3 are deposited on substrate 1 to form a layer 4 thereon.

[0012] The beam of a laser 5 is focussed in a focal point 6 on layer 4 using suitable focusing optics 7. The radiation energy of the laser light is absorbed by the nanoparticles, leading to a temperature increase above the melting point of the particles. The generated heat evaporates the solvent and melts the nanoparticles at least partially. When the heated nanoparticles are moved away from focal point 6, they cool down and solidify, leaving a solid structure 8.

[0013] While drops 3 are being deposited and laser 5 sinters or melts the particles into the solid structure, substrate 1 is being moved in respect to laser 5 and droplet generator 2. For this purpose, substrate 1 can e.g. be displaced by a positioning stage (not shown), while laser 5 and droplet generator 2 remain stationary.

[0014] Preferably, the drops 3 generated by droplet generator 2 impinge on substrate 1 at the position of focal point 6, which makes it possible to create a line shaped structure 8 along any direction.

[0015] Once structure 8 has solidified, any excess solvent and not sintered nanoparticles are removed; e.g. by washing. This post-processing step can be avoided by depositing a line-structure that is smaller than the focal point of the laser so that the deposit solvent is evaporated in its entirety.

[0016] The operation of drop generator 2 and laser 5 and the displacement of substrate 1 are preferably controlled by a computer 10.

[0017] For monitoring the formation of the structure 8, the apparatus can further be provided with a monitoring system, which comprises a stroboscope 11, a camera with microscope lens 12 and a framegrabber 13. The stroboscopic light source 11 is triggered e.g. in synchronicity with the release of the drops 3, thereby generating a standing picture of the drops arriving at focal point 6 in framegrabber 13.

[0018] In the following, some aspects of the procedure are described in more detail.

[0019] Nanoparticles, suspension:

[0020] The nanoparticles are preferably made of metal for forming a metallic structure. Gold has been found an especially suited material. As mentioned above, nanoparticles of gold show a melting point of 300 to 400°C at a diameter of 2.5 nm, which allows to form the desired structure at moderate temperatures.

[0021] The nanoparticles can also be made of a non-

metallic material. In particular, the present method also allows to form ceramic structures. Of particular interest are superconductive ceramics, which could be sintered with the present process without creating the excessive thermal stress that is responsible for the prohibitingly brittle behaviour of superconductive ceramic components.

[0021] A preferred "solvent" or, more accurately, suspension-fluid for the nanoparticles is toluene. Toluene has good wetting properties and its viscosity is suited for generating small droplets. Further preferred solvents are other organic solvents, such as terpineol or xylene, or water.

#### Droplet generator:

[0022] The droplet generator 2 can be any device suited for a controlled generation of the drops 3. Preferred is the application of a drop on demand device where a volume of the suspension is compressed by piezoelectric or thermal compression, thereby squirting one or more drops of the suspension through an opening onto the substrate. Piezoelectric compression or any other isothermal mechanical or electromechanical compression is preferred because it is suited for any suspension, while the evaporation process required in thermal compression (bubble jet method) can lead to contamination or clogging.

#### Laser light:

[0023] The wavelength of the laser light and the intensity at focal point 6 have to be selected according to the properties of the nanoparticles as well as according to the desired heating rate. For best efficiency, at least 80% of the laser light should be absorbed in layer 4.

[0024] Preferably, the exponential absorption coefficient of the suspension for the laser light is even higher, at least  $0.1 \mu\text{m}^{-1}$ , in particular at least  $1 \mu\text{m}^{-1}$ , which ensures that most of the laser light is absorbed close to the surface of layer 4. It has been found that the heat is transported through the whole depth of the layer, sintering or melting all nanoparticles in focal point 6.

[0025] The wavelength of the laser light is preferably chosen to be in a region of high absorption of the suspension. The laser can either be operated in continuous or pulsed mode.

[0026] The diameter of focal point 6 must be sufficiently small for forming even the finest parts of the desired structure. A typical diameter is less than  $500 \mu\text{m}$ , preferably less than  $100 \mu\text{m}$ .

[0027] Typical average laser powers at a displacement speed in the order of  $1 \text{ mm/s}$  are in the order of  $0.2 \text{ W}$  to  $2 \text{ W}$  with a focal point diameter of  $100 \mu\text{m}$ , resulting in intensities in the order of  $25$  to  $250 \text{ W/mm}^2$ .

#### Example:

[0028] In a preferred example, gold nanoparticles with a mean average size of  $2$  to  $5 \text{ nm}$  were suspended in toluene. The mass-fraction of gold in the solution was  $40\%$  of the total weight.

[0029] Droplets were generated with a drop on demand piezoelectric jetting device from Microfab Inc. This piezoelectric device consists of a reservoir and a capillary glass tube filled with the suspension. A piezoelectric material is deposited on the outer surface of the glass capillary. When a voltage pulse series is applied to the piezoelectric material, a volumetric change is induced to the fluid (and a corresponding pressure wave is generated within it) and a drop 3 will be ejected.

[0030] The drops 3 were deposited to form layer 4 as a line on a silicon wafer substrate by moving the substrate continuously at a speed of  $1 \text{ mm/s}$  with a positioning stage. The deposited layer 4 was simultaneously cured by light from an Argon ion laser at a wavelength of  $488 \text{ nm}$ , where the slurry had an absorption of less than  $1 \mu\text{m}^{-1}$ . The focal point 6 was located right behind the point where the drops impinged on the substrate 1. It had a diameter of approximately  $100 \mu\text{m}$ .

[0031] After cooling, the remaining structure consisted of solid, continuous, electrically conducting gold lines with an electrical conductance at least as good as that of bulk gold. The lines had a typical width of  $60$  -  $100 \mu\text{m}$ .

[0032] In the example mentioned above, substrate 1 was a silicon wafer. Other types of substrates can be used as well, such as substrates of glass or ceramic.

[0033] For expediting the melting or sintering of the nanoparticles, the substrate and/or the suspension can be heated to a temperature below the melting point of the nanoparticles, thereby decreasing the amount of energy required from the laser.

[0034] In the above examples, the liquid layer 4 has been formed by applying the drops 3 generated by droplet generator 2. Instead of a drop-wise application of the suspension, other coating methods, such as spin coating, can be used for producing layer 4. Again, the laser light is then used for forming the desired structure.

[0035] Instead of being present in the form of a regular suspension (i.e. a solid in liquid suspension), layer 4 may also be formed by a "solid suspension", i.e. the nanoparticles can be suspended in a solid matrix, e.g. by solidifying the "solvent" after spin coating by temperature decrease or partial evaporation. Alternatively, the nanoparticles can be suspended in a gas.

[0036] The heating and curing of the nanoparticles with laser light can take place while layer 4 is being formed, such as shown in the example above. It can also take place after the formation of layer 4.

[0037] The method described here can be used for forming any type of structure. Examples are conducting lines for interconnections on or to a semiconductor chip or for connecting a semiconductor chip to a substrate or to connector pins, metallic or non-metallic parts of Micro

Electromechanical Systems (MEMS) or superconducting structures.

[0038] A primary application of the present invention is for constructing gold lines for interconnections in electronics manufacturing, ranging from chip assembly packaging to flat panel display construction. The critical benefit to be harvested from the low melting and bonding temperatures of the gold nanoparticles is twofold: First, the printing of gold microline interconnections with a at-demand microdroplet generation technique is possible because one deals with a room temperature nano-suspension facilitating the application of piezoelectric ceramics with Curie temperatures of only a few hundred degrees Celsius. This would be impossible with molten gold at temperatures exceeding 1063 °C. Second, at the droplet deposition end, excess thermal stress and melting or burning of sensitive chip structures can be avoided. The method can be used under normal atmosphere environment yielding a fast, user friendly and cost effective interconnection manufacturing process appropriate for use in combination with a variety of delicate substrate materials.

#### Claims

1. A method for producing a structure on a substrate (1) comprising the step of applying nanoparticles of a material to form the structure (1) and characterized by the steps of melting the nanoparticles at least partially by exposition to laser light and solidifying the molten nanoparticles for forming the structure (8).
2. The method of claim 1 comprising the steps of focussing the laser light in a focal point (6) and translating the focal point (6) in respect to the substrate (1) for forming the structure.
3. The method of claim 2 wherein the focal point (6) has a diameter of less than 500 µm, in particular less than 100 µm.
4. The method of one of the claims 2 or 3 wherein the substrate (1) is moved for generating the structure.
5. The method of one of the preceding claims comprising the step of applying a suspension of the nanoparticles in a liquid to the substrate (1), and in particular of forming a layer (4) of the suspension on the substrate (1).
6. The method of claim 5 wherein the suspension is applied in drops (3) to the substrate (1) using a droplet generator (2).
7. The method of claim 6 comprising the step of generating the drops (3) by compressing a volume of
8. The method of one of the claims 2 to 4 and of one of the claims 5 to 7 wherein the drops (3) are deposited on the substrate (1) at the focal point (6).
9. The method of one of the claims 5 to 8 wherein the liquid is selected from the group comprising toluene, terpineol, xylene and water.
10. The method of one of the claims 5 to 9 wherein an exponential absorption coefficient of the laser light in the suspension is at least 0.1 µm<sup>-1</sup>, in particular at least 1 µm<sup>-1</sup>.
11. The method of one of the claims 5 to 10 wherein the suspension is deposited as a layer (4) on the substrate (1), wherein at least 80% of the laser light is absorbed in the layer (4).
12. The method of one of the preceding claims wherein the nanoparticles are of a metal, in particular of gold.
13. The method of one of the preceding claims wherein an average diameter of the nanoparticles is sufficiently small for reducing a melting point of the nanoparticles substantially below a bulk melting point of the material, and in particular wherein the average diameter is less than 100 nm, in particular less than 10 nm, preferably between 2 nm and 5 nm.
14. The method of one of the preceding claims wherein the structure is a superconducting ceramic material.
15. The method of one of the preceding claims further comprising the step of observing the production of the structure using a stroboscopic light source (11) and a camera (12), and in particular wherein the stroboscopic light source (11) is triggered in synchronicity with the application of drops (3) of a suspension of the nanoparticles to the substrate (1).
16. A structure producible by the method of one of the preceding claims.
17. Application of the method of one of the claims 1 - 15 for the production of electrical interconnections on and/or to semiconductor chips.

the suspension by piezoelectric or thermal compression and thereby squirting the drops through an opening onto the substrate.

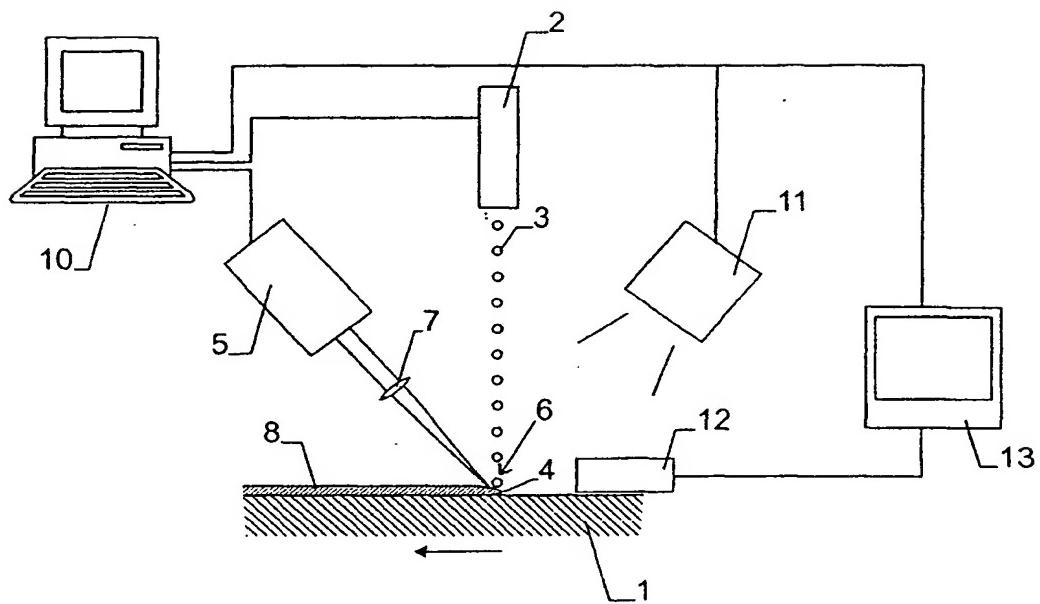


Fig. 1



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## EUROPEAN SEARCH REPORT

Application Number

EP 01 10 0537

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 07, 29 September 2000 (2000-09-29) -& JP 2000 104101 A (SANYO ELECTRIC CO LTD), 11 April 2000 (2000-04-11) * abstract * * paragraph '0012! - paragraph '0021!; figure 1 *	1-5, 9, 12, 13, 16, 17	H01L21/768 H05K3/10 H01L21/00
Y	EP 0 417 294 A (MAXIMOVSKY SERGEI NICOLAEVICH ;ZYBIN KIRILL PETROVICH (SU)) 20 March 1991 (1991-03-20)	1, 5-7, 12, 16, 17	
A	* the whole document *	4, 9	
Y, D	WO 00 10197 A (GOLDSTEIN AVERY N) 24 February 2000 (2000-02-24) * page 5, line 4 - page 8, line 9 * * page 10, line 22 - page 11, line 18 *	1, 5-7, 12, 16, 17	
A	WO 99 53738 A (KOCH HANS ;DIAGNOSTIKFORSCHUNG INST (DE); SEMMLER WOLFHARD (DE)) 21 October 1999 (1999-10-21) * the whole document *	1-17	
A	US 4 910 118 A (ADAIR PAUL C ET AL) 20 March 1990 (1990-03-20) * column 3, line 25 - line 29 * * column 4, line 13 - line 47; figures 5, 6 *	1-17	
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 03, 30 March 2000 (2000-03-30) -& JP 11 350107 A (ADVANCED MATERIALS PROCESSING INSTITUTE KINKI JAPAN), 21 December 1999 (1999-12-21) * abstract; figure 1 *	1-17	
	---	-/-	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	19 June 2001	Micke, K	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & member of the same patent family, corresponding document	
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## EUROPEAN SEARCH REPORT

Application Number  
EP 01 10 0537

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	<p>SHIVASHANKAR G V ET AL: "BIOMOLECULAR RECOGNITION USING SUBMICRON LASER LITHOGRAPHY"          APPLIED PHYSICS LETTERS, US, AMERICAN INSTITUTE OF PHYSICS, NEW YORK,          vol. 73, no. 3, 20 July 1998 (1998-07-20),          pages 417-419, XP000776741          ISSN: 0003-6951          * page 417, left-hand column, paragraph 1          - paragraph 2 *          * page 418, left-hand column, paragraph 2          *          * page 419, left-hand column, paragraph 2          - right-hand column, paragraph 1; figure 2          *</p> <p>-----</p>	1-17	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of compilation of the search	Examiner	
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19-06-2001

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 2000104101 A		11-04-2000	NONE		
EP 0417294	A	20-03-1991	CN	1045895 A	03-10-1990
			JP	3504910 T	24-10-1991
			WO	9011673 A	04-10-1990
WO 0010197	A	24-02-2000	AU	5560499 A	06-03-2000
WO 9953738	A	21-10-1999	DE	19817530 A	14-10-1999
			EP	1070444 A	24-01-2001
US 4910118	A	20-03-1990	JP	63259553 A	26-10-1988
JP 11350107 1 A			NONE		

**Attachment C**

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**CONFIRMATION NO. 8907**

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 MICHAELSON AND WALLACE  
 PARKWAY 109 OFFICE CENTER  
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 P O BOX 8489  
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**FILING RECEIPT**


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**Applicant(s)**

Constantine P. Grigoropoulos, Berkeley, CA;  
 Nicole Renee Bieri, Zurich, SWITZERLAND;  
 Dimos Poulikakos, Zollikon, SWITZERLAND;  
 Jaewon Chung; Albany, CA;

NOV 29 2003

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**Foreign Applications**
**If Required, Foreign Filing License Granted:** 11/25/2003

**Projected Publication Date:** To Be Determined - pending completion of Missing Parts

**Non-Publication Request:** No

**Early Publication Request:** No

**\*\* SMALL ENTITY \*\***
**Title**

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Method for producing a structure using nanoparticles

Preliminary Class

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